LXXXIV.—*The Absorption Spectra of Nicotine, Coniine, and Quinoline as Vapours, Liquids, and in Solution.*

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THE author has already presented the results of an investigation of the vapours of pyridine and some of its derivatives (this vol., p. 692). Since then, the vapours, the liquids, and solutions of nicotine, coniine, and quinoline have been investigated. The experimental methods employed in the study of the vapours are described in the earlier paper, and the methods for the study of the solutions have also been described before. The substances were redistilled several times before they were used.

Nicotine (α -pyridyl-N-methylpyrrolidine).—Hartley (*Phil. Trans.*, 1885, **176**, 471) examined the absorption of alcoholic solutions of this β -pyridine derivative, and found that with 0.367 gram in 36.7 c.c. of alcohol through a thickness of 1 mm. there was general absorption at about λ 2800; and through a thickness of 5 mm. the rays were absorbed at about λ 3132, but no band was observed. In the author's experiments with *N*/10-solutions, through 2 mm. thickness, the rays were absorbed at λ 2800; and, through 30 mm. thickness, at λ 3050; whilst for *N*/100-solutions, through 2 mm. thickness, the rays were absorbed at λ 2720, and, through 30 mm. thickness, at λ 2810, and no band was observed. But on examining *N*/1000-solutions, a band was discovered, and its absorption curve has been drawn (see Fig.). The general form of the curve is like that of pyridine (Hartley, *Trans.*, 1885, **47**, 685), but it is not so persistent. In this respect, its behaviour is similar to that of other pyridine derivatives. The weighting of the pyridine nucleus has also shifted the positions of the band and general absorption more towards the red end of the spectrum. The heads of the bands of pyridine and nicotine, expressed in oscillation frequencies, are:

Pyridine (Hartley)	3950
Nicotine	3820

The vapour of nicotine was examined under the following conditions of temperature and pressure in a tube 200 mm. long:

t° .	Pressure in mm.	
15°	750	All the rays were transmitted to Cd 2144; the latter was well marked.
60	850	All the rays were transmitted to Cd 2194.
100	926	The rays were transmitted to about λ 2390; the rays were then absorbed to Cd 2329; the Cd lines 2321, 2313, 2306, 2288, 2267, 2265 being visible.

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In another series of observations taken later, the following was observed :

t°	Pressure in mm.	
14°	757	All the rays were transmitted to Cd 2144.
100	933	The rays were transmitted to about λ 2400 ; the rays were then absorbed to Cd 2329, and the series of Cd lines to λ 2265 was well marked.

In order to increase the amount of vapour, one drop of the mixture was introduced in the absorption tube. The temperature

of the bath was raised to 100°, and the absorption of the vapour observed at the following pressures :

t°	Pressure in mm.	
100°	757	The rays were transmitted to Cd 2837 ; Cd 2748 was just visible.
100	627	The rays were transmitted to Cd 2837 ; Cd 2748 being visible.
100	27	„ „ „ „ λ 2820 ; Cd 2748 „ „

These observations indicate that (1) *N*/1000-alcoholic solution

of nicotine exhibits a band showing its relationship to pyridine; (2) the vapour of nicotine exhibits none of the series of narrow bands which have been observed by the author in pyridine vapour, but, as the temperature and pressure are increased, a strong absorption band is produced. The result is precisely similar to that observed in the vapours of the two dimethylpyridines and trimethylpyridine, and differentiates it from α -picoline vapour, which exhibited a few narrow bands, some of which are coincident with those of pyridine vapour (this vol., p. 692).

Coniine (α -N-propylpiperidine).—Hartley (Trans., 1885, **47**, 685) observed that alcoholic solutions of piperidine showed no bands in the ultra-violet, and that it was remarkably transparent. Coblentz (*Astrophys. J.*, 1904, **20**, 207) found a band in the ultra-red in the region of 3μ . The author has compared equimolecular solutions of piperidine and coniine, but no bands were observed in the ultra-violet, and the following numbers give the regions where general absorption begins:

Piperidine.

N/10-Solution ; through	2 mm. thick :	general absorption began at	λ 2185.
	30 " " "	" " "	" λ 2345.
N/100-Solution ; through	2 " " "	" " "	" λ 2130.
	30 " " "	" " "	" λ 2220.

The results are in agreement with Hartley's observations.

Coniine.

N/10-Solution ; through	2 mm. thick :	general absorption began at	λ 2570.
	30 " " "	" " "	" λ 3290.
N/100-Solution ; through	2 " " "	" " "	" λ 2180.
	30 " " "	" " "	" λ 2635.
N/1000-Solution ; through	2 " " "	" " "	" λ 2130.
	30 " " "	" " "	" λ 2265.

The vapour of coniine was also examined in a 200 mm. tube under the following conditions of temperature and pressure:

t° .	Pressure in mm.	
15°	740	All the rays were transmitted to Cd 2194.
30	784	" " " Cd 2194.
45	810	" " " Cd 2239.
60	840	" " " Cd 2265.
75	870	" " " Cd 2265 ; but they were weak between 2370 and Cd 2329.
90	900	The rays were transmitted to λ 2390, and after that they were absorbed ; only the Cd lines 2329, 2321, 2313, 2288, and 2265 being well marked.
100	916	The rays were transmitted to λ 2410 ; then they were absorbed, but the Cd 2329, 2321, 2313, 2288, and 2265 were again well marked.

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In another series of observations, a drop of the liquid coniine was placed in the absorption tube so that it contained more vapour, and the following series of observations was made:

t° .	Pressure in mm.	
100°	9	The rays were transmitted to Cd 2264, although they were scarcely visible between λ 2400 and the Cd line 2329.
100	309	" " " "
100	739	" " " "
17	9	The rays were transmitted to Cd 2194, which was well marked.
17	309	" " " "
17	739	" " " "

These results show that (1) alcoholic solutions of coniine exhibit no absorption bands, and that they are remarkably transparent. This result is exactly similar to that of piperidine solutions as first noted by Hartley; (2) the vapour of coniine shows none of the series of narrow bands like those observed by the author in the vapour of piperidine (*loc. cit.*); but, as before, by increased temperature and pressure, a weak absorption band is produced.

Quinoline.—Hartley (Trans., 1885, **47**, 685) has pointed out that an alcoholic solution of a synthetic preparation of this substance exhibited an absorption band between λ 317 and λ 310; and that a natural specimen gave three bands, the positions of which were λ 317— λ 310, λ 308— λ 303, λ 303— λ 289. The author has examined *N*/1000-solutions of freshly distilled quinoline, and finds three bands similar to these.

The vapour of quinoline was examined in a 200 mm. tube at the following temperatures and pressures:

t° .	Pressure in mm.	
15.5°	765	Complete transmission of rays to Cd 2144.
30	809	Transmission of rays to Cd 2144, although they were weak between λ 2620 and λ 2550.
45	835	The rays were transmitted to λ 2630, and then absorbed to about λ 2430 (the Cd 2573 being visible). From λ 2430, the rays were transmitted to Cd 2144.
60	865	The rays were absorbed between λ 2660 and λ 2380, and then transmitted to Cd 2144; Cd 2573 was just visible.
75	895	The rays were absorbed between λ 2700 and λ 2340, and then transmitted to Cd 2144.
90	925	The rays were absorbed between λ 2710 and Cd 2329. The Cd lines to 2144 were well marked, although weaker than at 895 mm. pressure.
100	941	The rays were absorbed between λ 2740 and Cd 2329; the latter was very weak, and the Cd lines beyond λ 2144 were well marked.

The vapour was also examined at a constant temperature of 14°, and under the varying pressures of 33 mm., 183 mm., 333 mm., 483 mm., 633 mm., and 763 mm., but no bands were observed. There was a complete transmission of rays to Cd 2144.

These results show that (1) an alcoholic solution of quinoline

exhibits three bands, as first noticed by Hartley; (2) the vapour of quinoline shows none of the various bands found by Hartley in the case of benzene vapour (*Phil. Trans.*, 1907, A, **208**, 475), and by the author in the case of pyridine vapour (this vol., p. 692), but it has one large band. The condensation of the benzene and pyridine nuclei to produce quinoline has completely destroyed the vibrations which produce the narrow absorption bands observed in the vapours of the two substances, but on increasing the temperature and pressure, a large absorption band is produced.

The spectra of nicotine, coniine, and quinoline in the liquid condition were also examined, and they were compared with those of pyridine, α -picoline, and piperidine. For this purpose one drop of each liquid was pressed between two thin plates of quartz, and these were firmly held in front of the slit of the spectroscope, whilst the light of the Cd spark was passed through for five minutes. No absorption bands were observed; and the following numbers represent the regions where general absorption began under these conditions:

Pyridine	λ 2780
α -Picoline	2830
Nicotine	2870
Quinoline	3340
Piperidine	2250
Coniine.....	2260

The remarkable transparency of liquid piperidine and coniine is very striking, and is similar to that of the solutions.

General Results.

The general results of these observations are:

(1) *N*/1000-alcoholic solution of nicotine exhibits an absorption band in the ultra-violet region of the spectrum analogous to that found in a solution of pyridine; the vapour of nicotine exhibits none of the series of narrow bands found in the vapour of pyridine; and the liquid nicotine, like that of pyridine, shows no selective absorption.

(2) *N*/10-, *N*/100-, and *N*/1000-alcoholic solutions of coniine show no bands of selective absorption, a result similar to that of solutions of piperidine; the vapour of coniine exhibits none of the series of bands found in the vapour of piperidine; and the liquid has no selective absorption, but, like piperidine, it is remarkably transparent.

(3) *N*/1000-alcoholic solution of quinoline has three bands in the ultra-violet, as observed by Hartley; the vapour of quinoline has no narrow bands analogous to those found in the vapours of benzene and pyridine, but only one large band; and liquid quinoline shows no selective absorption.

In the author's earlier paper on the absorption spectra of the vapours of pyridine and some of its derivatives, the presence of the numerous bands in pyridine was discussed from a consideration of the impacts of the molecules when in the vaporous condition (*loc. cit.*). The implied symmetry of such a molecule as pyridine or piperidine suggests a regular and rhythmical vibration or pulsation of the ring. When the substance is in solution or in the liquid condition, these vibrations or pulsations are constrained.

In solution, the solvent acts both as a constraint on the pulsations and as a barrier to the number of encounters. The fundamental vibrations of the molecule are predominant, and the result is shown in the absorptive effect on the radiant energy by the appearance of a single large band. In the liquid condition, these restraining influences are still more pronounced, and no band of selective absorption is observed. When, however, the substance is in the vaporous condition, the molecules are free from the restraining influences and, in addition to the fundamental vibrations producing strong absorption, other vibrations or pulsations are set in motion. The result is more complex and rhythmical, and it is manifested in a series of narrow bands which can be arranged in groups having equal differences of wave-lengths.

Now, solutions of piperidine exhibit an absorption band in the ultra-red, whilst in pyridine solutions the band is in the ultra-violet regions of the spectrum. The vapour of pyridine has a considerable number of narrow bands completely different from those observed in piperidine vapour. The liquids pyridine and piperidine show none of these bands, and the latter is remarkably transparent.

In coniine, nicotine, trimethylpyridine, the two lutidines, and α -picoline, the symmetry of the molecules is destroyed by the various side-chains, and to the restraining influence of the heavy side-chains on the vibrations of the nucleus are added the irregularity of the encounters. The result is that the nucleus does not vibrate in the same rhythmical manner. In α -picoline vapour, only a few of the narrow bands found in pyridine are observed; and, in the vapours of the two lutidines, trimethylpyridine, nicotine, and coniine, the narrow bands are completely absent. As regards quinoline, although there is an implied symmetry in the constitution of its molecule not possessed by the other substances, the pulsations characteristic of each separate nucleus are not maintained in combination, and the narrow bands shown by the vapours of benzene and pyridine are obliterated. The vapour of quinoline has one powerful absorption band, which is exhibited at increased temperatures and pressures.

In solutions of these substances, the series of narrow bands are

completely absent, and even the fundamental vibrations are considerably affected, as shown by the decreased persistence of the absorption band when the side-chains are increased in number, type, and weight. Whilst in the liquids the restraining influences are even more predominant, and the radiant energy is absorbed by the vibrating molecules, for there is no selective absorption.

In such investigations as these it is difficult to differentiate the possible effect of the radiant energy of the source of light. It is probable that light waves have an important influence on the vibrations of the molecules, and more particularly when the latter are in the vaporous condition, when they have more freedom of movement. If this influence is taken into consideration, it is more correct to say that the absorption bands are the result of such various forces as the radiant energy, the type of nucleus, the side-chains of the nucleus, the encounters of the molecules, and the constraint to which they are subjected as vapours, liquids, or in solution.

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